

Summary

A number of tetra-aryldiarsyls have been isolated in the solid state. Molecular weight determinations have shown that in the event any of the diarsyls used in our experiments undergo dissociation, the magnitude of the dissociation, at 80°, does not exceed 10%.

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THE EFFECT OF HEAT UPON *d*-ALPHA-PINENE¹

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In the paper on Port Orford cedar wood oil by Thurber and Roll² the suggestion is made that since the pinene from the oil studied did not form a trace of the inactive nitroso chloride, it is probable that the product is a *d*- α -pinene isomeric with the ordinary form of *d*- α -pinene which is isolated from American turpentine oil. The purpose of this paper is to present some evidence in support of that suggestion.

Smith³ determined the rate of racemization of *d*- α -pinene and calculated its heat of activation. He suggested that since α -pinene has two asymmetric carbon atoms "it would be expected that four isomeric modifications of the molecule, that is, two dextro and two levo forms, should exist." We would add that geometric isomers might also be expected because of the presence of the double bond. Many investigators have assumed that only two of these isomers, one dextro and one levo, are stable enough under ordinary conditions so that they may be isolated. However, a consideration of some of the common derivatives of α -pinene, such as the hydrochloride and the nitroso chloride, might lead one to a different conclusion. Thus we find that α -pinene nitroso chloride when prepared from highly optically active pinene is unstable in the air and is entirely different from the product prepared from inactive pinene. Also, pinene hydrochloride prepared from *d*-pinene is reported to be inactive, while that prepared from *l*-pinene is reported to have a negative rotation, the numerical value varying with the activity of the pinene used in the preparation. Likewise, the constants, such as melting points, reported in the literature for these compounds vary over a considerable range. It is clear that all of these differences which have been noted could be accounted for readily by assuming that the derivatives prepared, which show differences in properties, were made not from the same compound but from isomeric compounds. Rather than make such an assumption the differences noted are generally ascribed to differences in molecular aggregation or to degree of purity of the sample examined.

¹ Revised paper; original received February 23, 1928.

² Thurber and Roll, *Ind. Eng. Chem.*, 19, 739 (1927).

³ Smith, *THIS JOURNAL*, 49, 43 (1927).

The observations on inactive and levo pinene hydrochloride are more difficult to understand. If the dextro and levo α -pinenes were optical enantiomorphs one would expect their hydrochlorides to be identical. The best explanation at the present time of the above-mentioned observation is that pure *l*- α -pinene is difficult to prepare and, to the best of our knowledge, the hydrochloride of this pure product has never been prepared and studied.⁴ We expect to take up such a study in a later paper.

We have tried for some time to find a laboratory method which would enable us to obtain further evidence regarding the existence of the theoretically possible α -pinenes. It occurred to us that the method Smith used for the determination of the heat of activation should lead to interesting results when applied to samples of pinene which presumably might have different structures. Molecules of different structure would differ in energy content, and thus the amount of heat required to activate them should be different, even though the molecules were closely related structurally.

For the reason stated above we decided to determine the heat of activation of pinene from Port Orford cedar wood oil and of pinene from turpentine oil. A number of samples of turpentine were examined but the rotation of most of them was rather low. A sample with an observed rotation of 63.4° in a 1-dc. tube was finally chosen. This was sufficiently high so that satisfactory readings after partial racemization could be made. Pinene from Port Orford cedar oil in a tube of the same length has an observed rotation of 125.4°. Later we expect to be able to compare *l*-pinene from Oregon balsam with these two *d*-pinenes, and with the one examined by Smith. It is also hoped that a satisfactory analytical method for determining differences in the structures of α -pinenes may be developed.

Experimental Part

The pinene from Port Orford cedar wood oil was obtained in the manner described in a previous article by one of us.² It was purified for immediate use by fractionation over metallic sodium. The fraction having a boiling point of 156–157° was used in this work. The pinene from turpentine was purified in the same manner and the boiling point range was the same.

The method of procedure was similar to that outlined by Smith.³ The vapor, or vapor and liquid, of pinene was heated in a sealed tube for varying lengths of time at three different temperatures, namely, those of aniline, naphthalene and quinoline boiling freely under the atmospheric pressure prevailing during the course of an experiment. In order to drive the air from the reaction tubes without the use of highly efficient vacuum pumps and an absorption apparatus, an excess of the pinene was distilled from the tubes under a pressure of about fifteen millimeters. Since a practically constant boiling-point sample was used, this distillation should not affect

⁴ Lynn, THIS JOURNAL, 41, 361 (1919).

the composition of the sample remaining in the tubes. The tubes were sealed just before the liquid phase had disappeared. In making readings to note the change in optical activity, a polarimeter tube with a smaller diameter was used. Thus the volume of the liquid pinene condensing in the cold tube was sufficient so that it was not necessary to dilute the partially racemized product with a solvent to fill the polarimeter tube. The temperatures were corrected for variations from standard pressure by the usual formula for non-associated liquids. These corrections, per 10 mm. variation from standard pressure, amounted to 0.538° for aniline, 0.577° for naphthalene and 0.60° for quinoline.

The rate constants at each temperature were calculated according to the modified equation for a monomolecular reaction

$$K = \log_{10} (a_1/a_2) + (t_2 - t_1)0.8686$$

where a_1 is the polarimeter reading of original pinene, a_2 is the polarimeter reading of heated pinene and $t_2 - t_1$ is the length of the heating period in minutes. The results so calculated for both samples of pinene appear in Tables I and II.

TABLE I
PINENE FROM PORT ORFORD CEDAR OIL

Trial	Temp., °C.	Polarimeter readings	Time, minutes	$10^8 K$
A-1	184.2	37-33.2	2645	2.048
A-2	184.2	37-33.3	2830	1.862
A-3	183.9	37-33.6	2467	1.954
A-4	183.9	37-34.5	2475	1.413
A-5	184.6	37-32.7	2552	2.420
A-6	184.6	37-33.6	2746	1.755
A-7	184.2	37-34.5	2635	1.326
Av.	184.2	1.825
N-1	217.8	37-14.9	917	49.590
N-2	217.8	37-24.9	424	46.700
N-3	217.3	37-23.8	457	48.272
N-4	217.5	37-26.1	350	49.853
N-5	218.3	37-25.8	310	58.150
N-6	218.2	37-28	290	48.052
N-7	217.8	37-33.6	153	31.498
N-8	217.6	37-29.1	256	46.908
Av.	217.8	47.378
Q-1	236.7	37-24.6	80	255.1
Q-2	236.7	37-22.7	95	257.13
Q-3	236.7	37-24.5	84	245.38
Av.	236.7	252.54

It is at once evident that corresponding rate constants, K , for the two pinenes are approximately 100% greater in the case of the pinene from turpentine. This would indicate either a different structure for the two compounds or the presence in one of them of some catalyzing impurity, or possibly both influences combined to give rise to so decided a difference in

TABLE II
 PINENE FROM TURPENTINE OIL

Trial	Temp., °C.	Polarimeter readings	Time, minutes	10 ⁴ K
A-1	184.8	63.4-52.7	2170	4.259
A-2	184.7	63.4-52	2359	4.22
A-3	184.4	63.4-53.3	2160	4.017
Av.	184.6	4.159
N-1	218.45	63.4-36.7	318	85.95
N-2	218.0	63.4-44.9	233	74.04
N-3	217.95	63.4-44.7	240	72.81
Av.	218.1	77.6
Q-1	236.7	63.4-41	62	351.5

the reaction rate. In this connection it was noted that in all of the determinations at higher temperatures, especially in boiling quinoline, the pinene from turpentine became yellow, and in some cases a brown, resin-like substance, only partially soluble in the reaction mixture, formed. The latter solutions were too brown to examine in the polarimeter.

The heat of activation of pinene would presumably vary with the structure and be approximately independent of catalytic influences, since the percentage change due to catalysis would be very nearly the same at different temperatures. It has already been pointed out by Smith that "the only objectionable impurities in the substance measured would be other optically active substances racemizing at nearly the same rate as that of the substance under investigation." The heat of activation was calculated according to the Arrhenius equation

$$Q = 2.303RT_1T_2 \log_{10} (K_2/K_1) + (T_2 - T_1)$$

where Q is heat of activation in calories, R is the gas constant in calories, K_1 is rate constant at the lower temperature, T_1 absolute, and K_2 is rate constant at the higher temperature, T_2 absolute. The results so calculated for both samples of pinene appear in Tables III and IV.

 TABLE III
 PINENE FROM PORT ORFORD CEDAR OIL

Trials		Rate const., A	Rate const., N	Rate const., Q	Heat of act.
A _{1,2}	N _{1,2}	1.955	48.0885	42,570
A _{1,2}	N _{3,4}	1.955	49.0675	43,320
A _{3,4}	N _{1,2}	1.6835	48.0885	44,135
A _{3,4}	N _{3,4}	1.6835	49.0675	44,895
A _{1,2}	Q _{1,2,3}	1.955	252.54	42,947
A _{3,4}	Q _{1,2,3}	1.6835	252.54	43,986
N _{1,2}	Q _{1,2,3}	48.0885	252.54	43,691
N _{3,4}	Q _{1,2,3}	49.0675	252.54	42,231
Best value of K					
A (av.)	N (av.)	1.825	47.378	43,286
N (av.)	Q (av.)	47.378	252.54	44,083
A (av.)	Q (av.)	1.825	252.54	42,865
Average of all values obtained					43,411

TABLE IV
 PINENE FROM TURPENTINE OIL

Trials	Rate const., A	Rate const., N	Rate const., Q	Heat of act.
A ₁ N ₁	4.259	85.95	...	39,977
A ₁ N ₂	4.259	74.04	...	38,478
A ₂ N ₁	4.2015	85.95	...	40,040
A ₂ N ₂	4.2015	74.04	...	38,543
A ₃ N ₃	4.017	72.81	...	38,600
Best value of K				39,128
A (av.) N (av.)	4.159	77.6	...	39,072
N (av.) Q ₁	77.6	351.5	40,465
A (av.) Q ₁	4.159	...	351.5	39,535
Average of all values obtained				39,691

The letters and subscripts in these tables refer to the trial numbers in Table I.

Conclusions

Although the difference in the heat of activation of these two samples of pinene is not very great, it is beyond the limits of experimental error occurring in this work. The best value of the heat of activation for pinene from cedar wood oil is approximately 4300 calories higher than the corresponding value for pinene from turpentine oil. When all determinations are taken into account, the average difference between the heats of activation of the two pinenes is about 3700 calories. Thus one may feel justified in concluding that these two samples have different structures. Any difference in optical properties, providing the molecular structures of the two samples were the same, should not influence in any way the heat of activation, since dextro and levo forms of the same molecule have identical structures and, therefore, the same energy content.

Although we do not know the source of the pinene which Smith used,³ it evidently had the same structure as that of the pinene from Port Orford cedar oil, since the heats of activation of the two are approximately the same. The sample of pinene from turpentine appears to be a less stable isomer. It not only decomposes more readily, but its heat of activation is less than that of pinene from cedar oil.

It occurred to us that some interesting results should be obtained from a study of the nitroso chloride reaction of a sample of pinene before and after partial racemization. If it is only the high degree of optical activity that prevents the formation of a solid nitroso chloride, then after partial racemization there should be no difficulty in securing this nitroso chloride. On the other hand, if the two pinenes have different structures, and the ease of formation of the nitroso chloride depends only on the structure, then there should be no difference in the amount of this compound formed before and after racemization of the pinene.

To test the validity of this idea, a sample of the pinene from Port Orford cedar oil was heated to 200° in a closed evacuated tube for twenty-four

hours. Ten cubic centimeters of the product was allowed to react with an equal volume of amyl nitrite in 10 cc. of glacial acetic acid. Upon the addition of hydrochloric acid a solid precipitated out which had the characteristic melting point (112°) of pinene nitroso chloride. This result was unexpected. However, it was found on fractionation of the remainder of the heated pinene that only a small portion had the boiling point of the original pinene. Some change aside from racemization had evidently occurred during the heating process. The formation of the nitroso chloride in this instance, therefore, had no significance from the point of view of proving or disproving the question of the existence of isomeric α -pinene.

Because of this observed increase in boiling point of the heated pinene, it would appear possible that the measured rates of reaction may have been determined by some reaction other than simple racemization. To test this point further we combined corresponding portions of the partially racemized pinenes, fractionated them and examined the several fractions in the polarimeter. The results appear in Table V.

TABLE V
RESULTS OF FRACTIONATION EXPERIMENTS

	Volumes, cc.	Boiling range, $^{\circ}$ C.	Rotations
Port Orford cedar oil heated by boiling aniline	1	Below 155	..
	12	155-158	36.9
	3	158-169	33.9
	3	169-185	26.8
	3	Above 185	Gummy residue
Port Orford cedar oil heated by boiling naphthalene	1	Below 155	..
	5	155-158	33.0-34.0
	5	158-169	30.1
	5	169-185	22.0
	3	Above 185	Gummy residue
Turpentine oil heated by boiling aniline	1	Below 155	..
	5	155-158	19.6
	5	158-169	17.5
	2.5	169-185	..
	2	Above 185	Gummy residue

It will be noted that the greater portion of each sample distilled above 159° , indicating the presence of new compounds other than racemic pinene. However, the fraction which most nearly approximates the boiling point of pure pinene has a rotation approximating that of the original unheated pinene. The rotations given are the observed ones in all cases. The corresponding values for unheated pinene are 37 for the cedar oil, and 18.7 for the turpentine oil. It seems likely that a more thorough fractionation of a larger sample of the heated pinene would have given a pinene fraction with the same rotation as that of the unheated portion. We were unable to make this fractionation because of the small amount of material avail-

able. The observed rotation of the heated pinene samples is the average of the rotations of the several fractions appearing in the table.

It would seem, then, that the value which we have been measuring is the rate of rearrangement of pinene to other compounds, rather than the rate of racemization only. Smith³ also must have been measuring the same value. Smith's interpretation of his results would then not be correct unless the decomposition was preceded by racemization, and the latter was the slower reaction.

In any event the results show that the two pinenes which we have examined are different, and that the one from Port Orford cedar oil is evidently similar in structure to that studied by Smith.

Summary

The rates of decrease in optical activity at three different temperatures of pinene from Port Orford cedar oil and of pinene from turpentine have been determined. The rate constant for the latter is practically twice as great as for the former.

Assuming the decrease in optical activity to be due to racemization, the heats of activation of these two pinenes have been calculated. The value obtained for pinene from turpentine is approximately 3700 calories less than that for pinene from cedar oil.

It is suggested that only a difference in structure between the two pinenes could explain all of the experimental results reported. Differences in structure of α -pinene molecules would account for at least part of the peculiar and conflicting reactions of α -pinene which have been observed and reported.

When *d*- α -pinene is heated *in vacuo* the major portion is converted to compounds with higher boiling points than the original pinene.

The rate of reaction measured may be either the rate of racemization or the rate of rearrangement, depending upon which reaction is the slower.

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